[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Manufacture of Chlorhydrins and Ethers thereof.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of organic compounds and more particularly the manufacture of chlorhydrins from di- or other polyhydric alcohols.

It has been found that an improved manufacture of chlorhydrins may be obtained by treatment of the di- or polyhydric alcohol with hydrochloric acid, generated in the presence of the said alcohol. Any suitable method may be adopted for the generation of hydrogen chloride in the presence of the alcohol, for example, the action of sulphuric acid upon sodium chloride. However, other salts of hydrochloric acid or other acids may be used. The salts used may be capable of forming insoluble sulphates and other insoluble salts with the acids. In these circumstances, after the completion of the chlorination, the insoluble sulphate or other salt may be removed by filtration, and the chlorhydrins recovered by distillation under reduced pressure.

According to this invention glycol may be chlorinated to yield ethylene chlorhydrin and glycerol may be so treated as to yield its chlorhydrins. Mono- and di-chlorhydrins may be obtained. Furthermore the isomeric forms of the mono- and di-chlorinated compounds may also be obtained.

Although the invention is applicable generally to the manufacture of chlorhydrins from polyhydric alcohols it is best typified by reference to the preparation of monochlorhydrins from glycerol. It must be understood, however, that this particular description in no way limits the scope of the invention.

The initial reactants may, for example, comprise glycerol and sodium chloride, It will be found preferable in this method to use a quantity of sodium chloride in excess of that which is equivalent to the sulphuric acid to be used. Suitable means may be adopted to bring about constant and uniform agitation of the reactants during chlorination of the glycerol. Somewhat diluted sulphuric acid may be introduced into the reaction mixture, contained in a closed or pressure vessel, in such a way as to ensure steady evolution of hydrogen chloride. During the first stages of reaction it is advisable to apply at the most a gentle heat to the reaction vessel as considerable quantities of hydrogen chloride are evolved.

After some time when the generation of hydrogen chloride has considerably subsided the mixture may be more strongly heated to a temperature slightly above 100° C. for a further longer period. Small quantities of acetic acid (e.g. up to about 10% of the glycerol) may be added to the reactants. The reaction, however, proceeds quite smoothly without such addition. Acetic acid, if employed, is preferably used in quantities of from 1—2% calculated on the weight of the glycerol.

After heating to complete chlorination the reactants may then be distilled at ordinary pressures to a temperature of about 140° C. The monochlorhydrins or the major part thereof remain in the still and may be recovered by fractional distillation under reduced pressure.

The invention also includes the manufacture of the chlorhydrins in the form of their ethers. Thus where the conditions of manufacture are such as to promote etherification, for example where the reactants contain sulphuric acid in excess of the amount required for the generation of the hydrogen chloride, chlorhydrin ethers may be produced by condensation of two or more molecules of the chlorhydrin.

Dated this 14th day of July, 1932.

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[Price 1/-]

COMPLETE SPECIFICATION.

Manufacture of Chlorhydrins and Ethers thereof.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of organic compounds and more particularly the manufacture of chlorhydrins from di- or other polyhydric alcohols.

It has been found that an improved manufacture of chlorhydrins may be obtained by reacting on a di- or other polyhydric alcohol with hydrochloric acid generated in the presence of the said alcohol. Thus glycol may be treated so as to yield ethylene chlorhydrin and glycerol treated so as to yield mono- and di-chlorhydrins. Chlorhydrins of other polyhydric alcohols, e.g. erythritol, mannitol or polyglycerols, may likewise be obtained.

Any suitable method may be adopted for the generation of the hydrogen chloride. It is preferably formed by the action of an acid upon a chloride, for example sodium chloride. Preferably mineral acids are used, for example sulphuric acid or phosphoric acid. Other chlorides which may be employed are potassium chloride, and calcium or barium chloride, and such chlorides may form with the reacting acids salts which may or may not be water-soluble. The reaction mixture may also contain other substances which facilitate the reaction or improve the yield. Thus for example acetic acid may be employed in quantities up to about 10% (preferably 1—2%) calculated on the weight of the polyhydric alcohol. The reaction may be carried out under pressure, or, again a reflux apparatus may be employed. Means are preferably employed to bring about agitation of the reactants during chlorination, e.g. by the use of mechanical stirring devices. When the reaction is effected under pressure relatively low pressures are in general preferable, e.g. pressures of 2—3 atmospheres.

When the hydrogen chloride is generated by introducing sulphuric or other acid into a vessel containing the polyhydric alcohol and a suitable chloride, addition of the acid is preferably carried out gradually, and in the case of a reaction carried out under pressure a suitable device should be employed which will prevent any substantial loss of pressure during introduction of the acid.

Preferably hydrogen chloride is generated in the reaction mixture by the gradual introduction of sulphuric acid into the vessel containing the polyhydric alcohol and sodium chloride or other suitable chloride. In general it is desirable to carry out the earlier stages of the reaction at a relatively low temperature, e.g. 50—60° or 70° C., and during the later stages of the reaction, e.g. when sufficient acid has been added to evolve the quantity of hydrogen chloride necessary to effect the desired degree of chlorination, gradually to raise the temperature and complete the reaction at a higher temperature, e.g. 100—110° C. or more.

On completion of the reaction the mixture may be distilled at ordinary pressure to remove water and other volatile constitutes and then fractionally distilled under reduced pressure in order to obtain the chlorhydrins. Thus glycerol mono-chlorhydrin may be collected between 114—120° C. at 14 mm. pressure. If desired the whole distillation may be effected under reduced pressure. Any acid present in the reaction mixture may be neutralised before fractionation, e.g. by means of sodium carbonate, and insoluble matter may be separated, e.g. by filtration.

The invention also includes the further treatment of the chlorinated compounds which have been produced in the manner aforesaid so as to yield the chlorhydrin ethers. Thus the reaction medium obtained after production of the chlorhydrins may be raised to a higher temperature, e.g. 200—250° C., and heated for several hours, and on completion of the reaction the reaction product may be fractionated, preferably under reduced pressure, to separate the chlorhydrin ethers formed. Preferably the reaction is effected in the presence of a suitable condensing agent, e.g. sulphuric or hydrochloric acid, though if excess hydrochloric acid is present on completion of the reaction for the manufacture of the chlorhydrins formation of the ethers may be carried out at the higher temperature without the addition of further condensing agent. Alternatively the chlorhydrins may be partially or completely separated from other substances, e.g. by filtration and/or fractional distilation, before carrying out the process for the production of the ethers.

The following examples are given in order to illustrate the invention, but it is to be clearly understood that the invention is not limited in any way thereto.

EXAMPLE 1.

180 parts by weight of sodium chloride, 250 parts by weight of glycerol and 5 parts by weight of glacial acetic acid are introduced into an autoclave fitted with a stirrer and a pressure gauge. The temperature is raised to about 50 to 60° C. and 90% sulphuric acid is slowly introduced through a suitable device adapted to prevent loss of pressure, the rate of introduction of the acid being regulated so as to maintain the pressure at about 1½—2 atmospheres absolute. When sufficient acid has been introduced to convert all the sodium chloride to sodium sulphate, the addition of acid is stopped and the temperature is gradually raised to 100°—110° C. and maintained at that temperature for about 2 to 3 hours. During the progress of the reaction the contents of the autoclave are well stirred. On completion of the reaction, the reaction liquors may be fractionated and the mono-chlorhydrin collected between 114—120° C. at a pressure of 14 mm.

EXAMPLE 2.

Equal weights of glycol and sodium chloride are introduced into an autoclave, and chlorination of the glycol is carried out as described in the preceding Example.

EXAMPLE 3.

The following example describes the production of the chlorhydrin ether from the ethylene chlorhydrin obtained according to Example 2. The reaction liquors obtained on the completion of the reaction according to Example 2 are heated with about 6% of sulphuric acid, calculated on the weight of glycol originally employed, the temperature being raised slowly to about 200 to 250° C. and maintained at that point for about 3 hours. The reaction liquors are then separated by fractional distillation.

The chlorhydrin of example 1 may be converted into the corresponding chlorhydrin ether in a similar manner.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the manufacture of chlorhydrins, comprising reacting a di- or other polyhydric alcohol with hydrogen chloride generated in the presence of said alcohol.

2. Process for the manufacture of glycerol chlorhydrins, comprising reacting glycerol with hydrogen chloride generated in the presence of the glycerol.

3. Process for the manufacture of ethylene chlorhydrin, comprising reacting glycol with hydrogen chloride generated in the presence of the glycol.

4. Process according to any of Claims 1—3 in which hydrogen chloride is generated by action of a chloride and a mineral acid.

5. Process according to Claim 4 in which sulphuric acid is employed.

6. Process according to any of the preceding claims in which the reaction is effected under a superatmospheric pressure not exceeding 3 atmospheres.

7. Process according to any of the preceding claims wherein the temperature is maintained at 50—70° C. during generation of the hydrogen chloride, and is then gradually raised to 100°—110° C. to complete the reaction.

8. Process for the manufacture of chlorhydrins substantially as hereinbefore described.

9. Chlorhydrins of glycol or other polyhydric alcohol whenever prepared or produced by the methods or processes of manufacture particularly described and ascertained or by their obvious chemical equivalents.

10. Process for the manufacture of chlorhydrin ethers wherein chlorhydrins are obtained according to any of the processes of Claim 1—8 and are further heated at increased temperatures.

11. Process according to Claim 10 wherein heating is effected in the presence of sulphuric acid.

12. Process for the manufacture of chlorhydrin ethers substantially as hereinbefore described.

13. Chlorhydrin ethers whenever prepared or produced by the methods or processes of manufacture particularly described and ascertained or by their obvious chemical equivalents.

Dated this 12th day of July, 1933.

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